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## CADMIUM, GALLIUM, AND GERMANIUM RESOURCES IN VIRGINIA

Palmer C. Sweet and William F. Giannini

### INTRODUCTION

Cadmium, gallium, and germanium are metallic elements present in small amounts in various metallic mineral deposits, their associated mine tailings, and in coal ash. Based on many mining company requests regarding information on cadmium, gallium, and germanium occurrences in Virginia, basic sampling was undertaken to determine if potentially economic deposits of these elements might occur in former mined areas and in known deposits. Samples were collected and analyzed from the following sites: ore on the dumps and mine tailings at the former Tri-State Zinc Co., Bowers-Campbell mine near Timberville, Rockingham County; zinc-lead tailings at the former New Jersey Zinc Co. mine in Austinville, Wythe County; and from gossan developed on base-metal sulfide deposits (Zones 18 and 24) near Andersonville, Buckingham County (Figure 1). At this last site, additional samples were taken from three core-holes. Samples were analyzed by XRAL Activation Services, Ann Arbor, Michigan by the multi-method, multi-element quantitative analyses method in a package of 57 different elements plus loss on ignition (LOI). The samples were analyzed for the following elements: Cd, Ga, Ge,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , CaO, MgO,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{Fe}_2\text{O}_3$ , MnO,  $\text{TiO}_2$ ,  $\text{P}_2\text{O}_5$ , Ag, As, Au, B, Ba, Be, Bi, Br, Cl, Co, Cr, Cs, Cu, Hf, Li, Mo, Nb, Ni, Pb, Rb, S, Sb, Sc, Se, Sn, Sr, Ta, Th, U, V, W, Y, Zn, Zr, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Pt, and Pd. Various methods were used in analyzing the samples: cadmium by ICP (inductively coupled plasma) with a detection limit of 1 ppm; gallium by XRF (X-ray fluorescence) with a detection limit of 3 ppm; germanium by DCP (direct current plasma) with a detection limit of 10 ppm; and silica ( $\text{SiO}_2$ ) by X-ray fluorescence. Additionally, occurrences of germanium,

noted in analyses of coals sampled by the Division, are provided in this report.

Analyses were made for gold (Au) and silver (Ag) from all the sites. At the Bowers-Campbell mine, the highest values were 2 ppb gold and 0.6 ppm silver; at the New Jersey Zinc Co. mine, 3 ppb gold and 2.2 ppm silver; at base-metal sulfide Zone 18, 76 ppb (.076 ppm) gold and 11 ppm silver, and from Zone 24, 590 ppb (.59 ppm) gold and 35 ppm silver. Data on the other elements are available at the Division of Mineral Resources office in Charlottesville.

1. Bowers-Campbell mine
2. New Jersey Zinc Co. mine
3. Sulfide zones 18 and 24

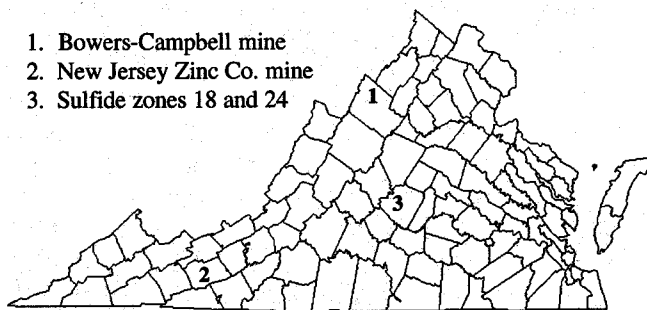


Figure 1. Sample locations for cadmium, gallium, and germanium.

### METALLIC ELEMENTS INVESTIGATED

#### CADMIUM

Cadmium is a tin-white, malleable metal that takes a high polish. The greatest demand for cadmium is for nickel-cadmium batteries (55 %). The remaining cadmium is used for industrial purposes in coating and plating (14 %); in pigments

(16 %), in plastics and synthetic products (10 %), and in alloys and other uses (5 %). Nickel-cadmium battery use could increase with the use of electric vehicles.

Since cadmium minerals do not occur in economic quantities as mineral deposits, they are produced as a byproduct from zinc ores, lead ores or from complex copper-lead-zinc ores. Cadmium also occurs in the mineral greenockite ( $\text{CdS}$ ). Zinc concentrates containing 0.3 percent (3000 ppm) cadmium are considered economical. One thousand tons (2,204,600 pounds) of cadmium were produced in the United States in 1994 (U.S. Bureau of Mines, 1995). Primary cadmium was recovered as a byproduct of smelting domestic and imported zinc concentrates by three companies: Big Zinc Corp., Sauget, Illinois, Zinc Corp. of America, Bartlesville, Oklahoma, and Jersey Miniere Zinc Co. in Clarksville, Tennessee. ASARCO Incorporated in Denver, Colorado recovers cadmium from its lead smelter baghouse dust. Some secondary cadmium is produced by remelting scrap generated during primary production, from remelting of cadmium-containing alloy scrap, from spent nickel-cadmium batteries and from dust generated during the operation of electric arc furnaces used in the steel-making industries.

The value of the metal was \$1.60/pound in June, 1995, down from \$6.28/pound in 1988 (Peter Kuck, 1995, personal communication). Imported cadmium metal totaled about 196 metric tons (431,660 pounds) in 1993; Canada, Belgium, Mexico, France, and Germany are the leading countries exporting to the United States.

### GALLIUM

Gallium is a silvery-gray or bluish-white semi-metal that commonly occurs with oxide minerals, mainly limonite-goethite (gossan), derived from weathering of copper-lead-zinc sulphide ores. Deposits containing 0.036 percent (360 ppm) gallium have been worked commercially. Gallium has a unique property of being liquid near room temperature (melting at about 30 degrees C). About 54 percent of gallium metal is used in optoelectronic devices such as light-emitting diodes, laser diodes, photodetectors, and solar cells. Other uses are for integrated circuits in defense applications and high-performance computers, speciality alloys and other applications.

In 1985, the Apex mine, near Shivwits in southwestern Utah, was opened by St. George Mining Corp., a subsidiary of Musto Explorations Ltd., Vancouver, Canada. This was the world's first primary producer of gallium and germanium dioxide in 1986 (U.S. Bureau of Mines, 1986). The ore is defined as a goethite-limonite-hematite zone, part of a solution-collapse breccia pipe in Pennsylvanian-age limestone. It contains local concentrations of jarosite (potassium iron-magnesium silicate), azurite, malachite, and other supergene copper, iron, lead, and zinc minerals (Bernstein, 1986; U.S. Bureau of Mines, 1986). The ore is oxidized to a depth of at least 1395 feet below the surface. Gallium is concentrated in the jarosite (to 0.7 percent) and as much as 2 percent in the limonite. Germanium is concentrated mainly in goethite (as much

as 0.5 percent), hematite (as much as 0.7 percent), and in limonite (as much as 0.5 percent). Harbuck and others (1991) note that some of the germanium is associated with quartz and is difficult to recover. In 1986, St. George Mining Corp. estimated the proven reserves to be 180,000 tons of ore containing 0.042 percent gallium and 0.115 percent germanium. During 1986, 1650 pounds of gallium and 5621 pounds of germanium were produced from the mine (U.S. Bureau of Mines, 1986). In 1987, no germanium was produced but gallium production increased until September 1, when the mine closed because of technical problems with the germanium refinery, weak gallium prices and financial difficulties. Hecla Mining Co. of Idaho purchased the operation in March, 1989. Harbuck and others (1991) investigated the use of a sulfuric acid leach technique for extracting gallium and germanium from the Apex mine ore. The study indicated that by using a two-stage counter-current sulfuric acid leach system, optimum extraction of gallium increased to over 95 percent while germanium extraction reached a peak of 71 percent after which it decreased to less than 50 percent. The percentage of increase of germanium extraction is low because some of the ore is locked in quartz, where it can not be attacked and leached by the acid. The mine has not reopened.

There was no primary domestic production of gallium in 1994, according to the U.S. Bureau of Mines. Two companies in Oklahoma and Utah recovered gallium from scrap and impure gallium metal. The Specialty Materials Division of Eagle-Picher Industries Inc., Quapaw, Oklahoma recovered and refined gallium from primary and secondary source materials, including reprocessing of scrap metal. The Hecla Mining Co., located near Shivwits, Utah, produced some gallium from scrap generated during the production of gallium arsenide. The average value of gallium metal in 1994 was \$180/pound.

### GERMANIUM

Germanium is a rare, grayish-white, semiconducting metalloid that occurs with oxide minerals, mainly limonite-goethite (gossans) derived from weathering of copper, lead and zinc ores, and in coal. The metal has exceptional properties as a semiconductor. The major uses of germanium are infrared optics, 24 percent; fiber-optic systems, 35 percent; detectors, 10 percent; semiconductors (including transistors, diodes, and rectifiers), 10 percent; and other applications such as catalysts, phosphors, and metallurgical uses.

Concentrations of 0.089 percent (890 ppm) germanium have been worked economically in the past. Production of germanium from three refineries amounted to almost 10 metric tons (22,000 pounds) in 1994 (U.S. Bureau of Mines, 1994). This figure is half of the reported production for 1989. Kawecki Berylco Industries Inc., a division of Cabot Corp. in Revere, Pennsylvania and Atomergic Chemetals Corp. in Plainview, New York both produced germanium from industry generated scrap metal and from imported concentrates. In Quapaw, Oklahoma, Eagle-Picher Industries Inc.'s Speciality Materi-

als Division recovers primary germanium from zinc smelter residues. They also reprocess scrap metal. The Jersey Miniere Zinc Co. in Clarksville, Tennessee produces germanium-rich residues by processing zinc ores from the nearby Elmwood-Gordonville mines. Most of these germanium-rich residues are shipped to Belgium for recovery and refining (U.S. Bureau of Mines, 1995).

Germanium metal is presently valued at \$482/pound (U.S. Bureau of Mines, 1995). Imports of estimated germanium content was approximately 14.8 metric tons (32,560 pounds) in 1993; the majority of the material was imported from Ukraine, China, Russia, Germany, and Belgium (U.S. Bureau of Mines, 1994).

## SAMPLE SITES AND ANALYTICAL RESULTS

### BOWERS-CAMPBELL MINE

The Bowers-Campbell mine is located just northwest of Timberville in Rockingham County. Tri-State Zinc Company began exploration at this site in 1951 (Hayes, 1960) and mining began in May, 1956 and continued until July, 1963, at which time the mine was 475 feet deep. In April, 1965, the Timberville Lime Co. began marketing the mine tailings for use as agricultural lime, which continues to the present time.

The zinc ore is found in a mineralized collapse breccia composed of dolomite in the Ordovician-age Beekmantown Formation. Sphalerite, along with some pyrite, was the only economic mineral in the breccia. The minerals galena (PbS) and greenockite (CdS) are present in the wall rock. Greenockite in the dumps/stockpile and the zinc mine tailings were the targets for sampling on the site.

Four samples were taken on the mine property. The locations are shown in Figure 2 and the analyses to determine cadmium, gallium, germanium, and silica present are shown in Table 1. Sample descriptions follow:

Sample #1 Composite of a 6-foot vertical channel sample from the tailings pile (Figure 3).

Sample #2 Composite of 2 grab samples of sphalerite, gray and white (vein) dolomite and some greenockite from stockpile (Figure 4).

Sample #3 Composite of 3 grab samples of sphalerite, gray and white (vein) dolomite, sphalerite in breccia, with no visible greenockite from stockpile (Figure 4).

Sample #4 Composite of 4 grab samples of sphalerite in brecciated dolomite with greenockite from stockpile (Figure 5).

Table 1. Quantities of cadmium, gallium, germanium (all ppm) and silica (%) at the Bowers-Campbell mine.

	SAMPLES			
	1	2	3	4
CADMIUM	4	560	1200	3000
GALLIUM	19	<3	<3	<3
GERMANIUM	<10	10	40	20
SILICA	37.0	4.90	3.57	1.93

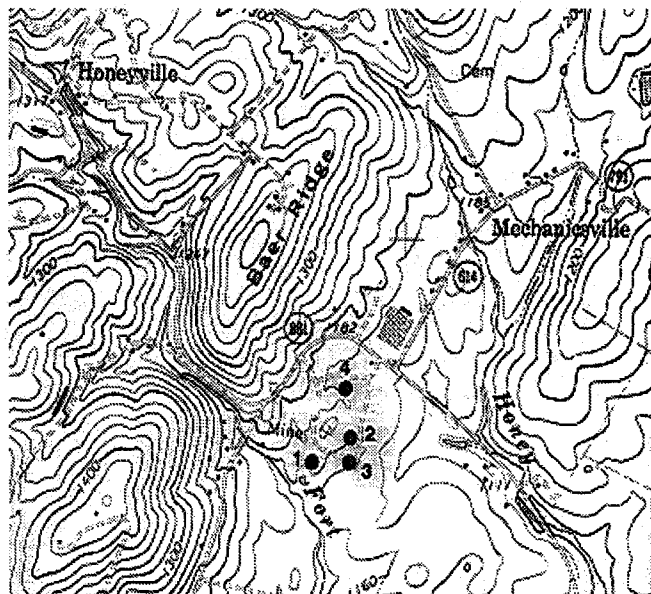


Figure 2. Location of sample sites at the Bowers-Campbell mine, Timberville 7.5-minute quadrangle, Rockingham County.



Figure 3. Zinc tailings (sample # 1) at the Bowers-Campbell mine.

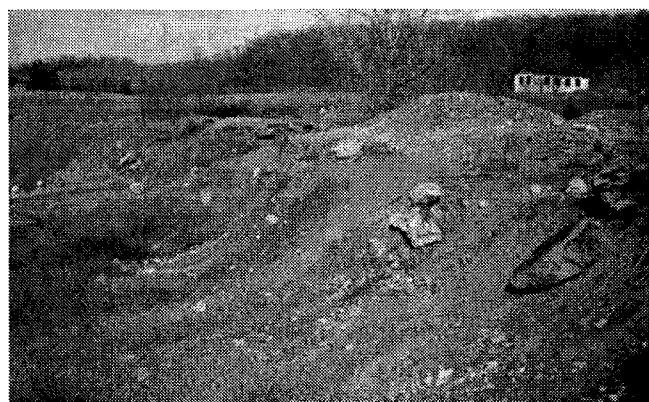


Figure 4. Old stockpile just north of the old shaft, samples # 2 and 3, Bowers-Campbell mine.

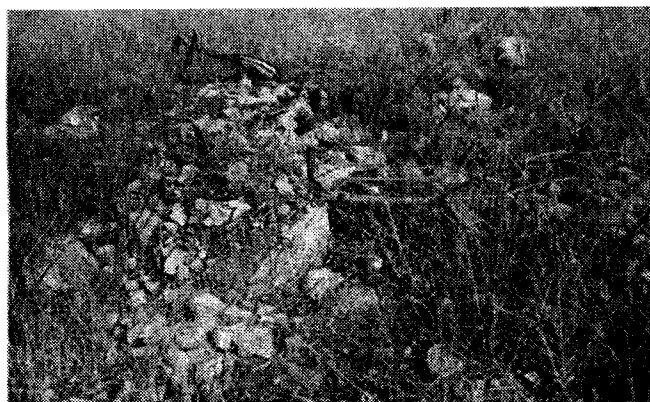


Figure 5. Old stockpile just south of scalehouse, location of sample #4, Bowers-Campbell mine.

#### NEW JERSEY ZINC CO. MINE

The zinc-lead deposit located at Austinville, Wythe County, was originally opened in 1756. The sphalerite and galena are present in brecciated Shady Dolomite. The present mine was last operated by The New Jersey Zinc Co. in November, 1981. The large tailings pile (approximately 5 million tons in 1992) is presently being marketed as agricultural material by the James River Limestone Co., Inc. (Sweet, 1994)

Eleven samples were taken: ten from the tailings pile and one from residuum over the country rock. The sample locations are noted in Figure 6, and the quantities of cadmium, gallium, germanium, and silica are displayed in Table 2. Descriptions are as follows:

Samples #1-9 Composite of sample taken from 8" to 10" holes in tailings pile.

Sample #10 Composite of 5-foot vertical section from tailings pile (Figure 7).

Sample #11 Composite of 5-foot residuum sample overlying dolomite.

Table 2. Quantities of cadmium, gallium, germanium (all ppm), and silica (%) at the New Jersey Zinc Co. mine.

	SAMPLES										
	1	2	3	4	5	6	7	8	9	10	11
CADMIUM	10	8	9	9	8	11	7	9	7	5	9
GALLIUM	13	14	15	15	13	12	14	59	27	14	15
GERMANIUM	<10	20	<10	<10	<10	<10	<10	<10	20	10	<10
SILICA	3.23	3.17	3.82	2.94	3.13	2.77	2.87	2.84	2.81	2.00	29.4

#### BUCKINGHAM COUNTY SULFIDE ZONES 18 AND 24

The sulfide district in Buckingham County, near Andersonville, contains two documented ore bodies, named Zones 18 and 24, that contain significant amounts of zinc and copper along with minor amounts of silver; gold occurs in trace amounts. Gossans occur over both of the zones and represent a hydrated oxide of iron over the sulfide bodies of pyrite and base met-als. The gossans were the target to determine the presence of cadmium, gallium, and germanium resources.

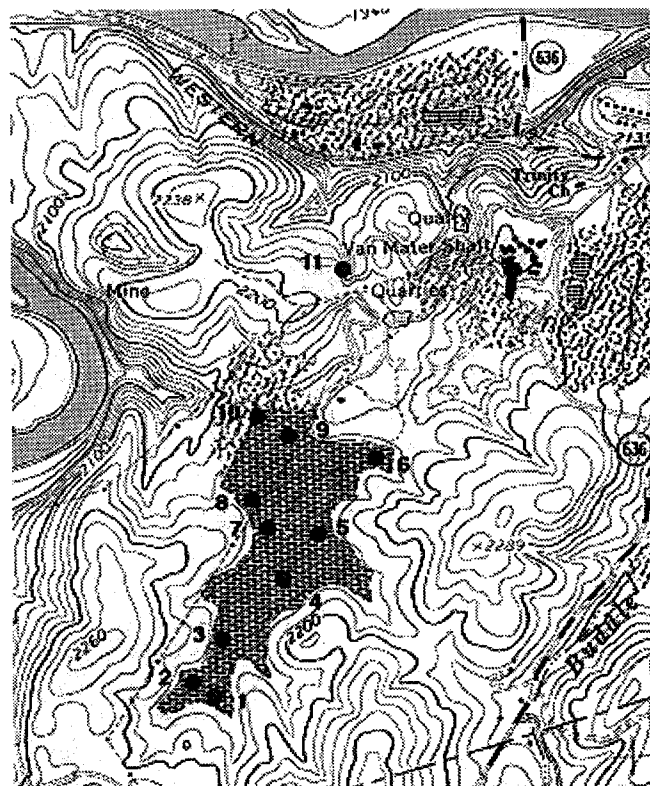


Figure 6. Location of sample sites at the New Jersey Zinc Co. mine, Austinville 7.5-minute quadrangle, Wythe County.

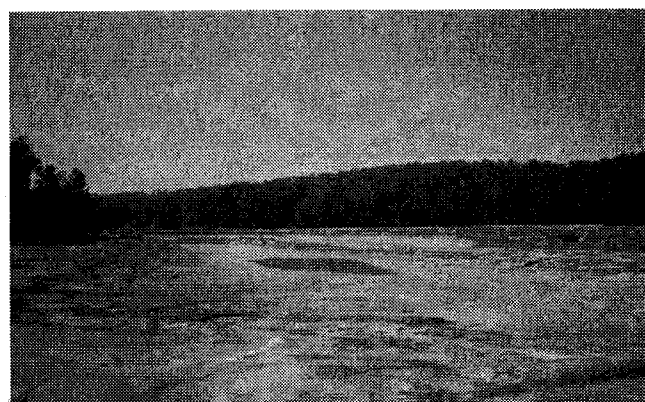


Figure 7. Zinc-lead tailings pile at the New Jersey Zinc Co. mine (Photograph taken in 1992).

Three samples were taken in Zone 18 and 30 samples in Zone 24 (Figure 8). In Zone 18, samples of gossan were taken normal to the regional strike of the body; sample # 1 for 150 feet, sample # 2 for 83 feet and sample #3 for 95 feet. In Zone 24, samples were taken approximately in a northwest-southeast direction along lines 2W, 2E, and 6E, as shown in Figure 9 (from Young, 1981). Samples were taken about 35 feet apart and consist of 1 to several pieces of gossan float at each site (Figures 10-12). Results are displayed in Table 3.



Figure 8. Location of sample sites in sulfide Zones 18 and 24, Andersonville 7.5-minute quadrangle, Buckingham County.

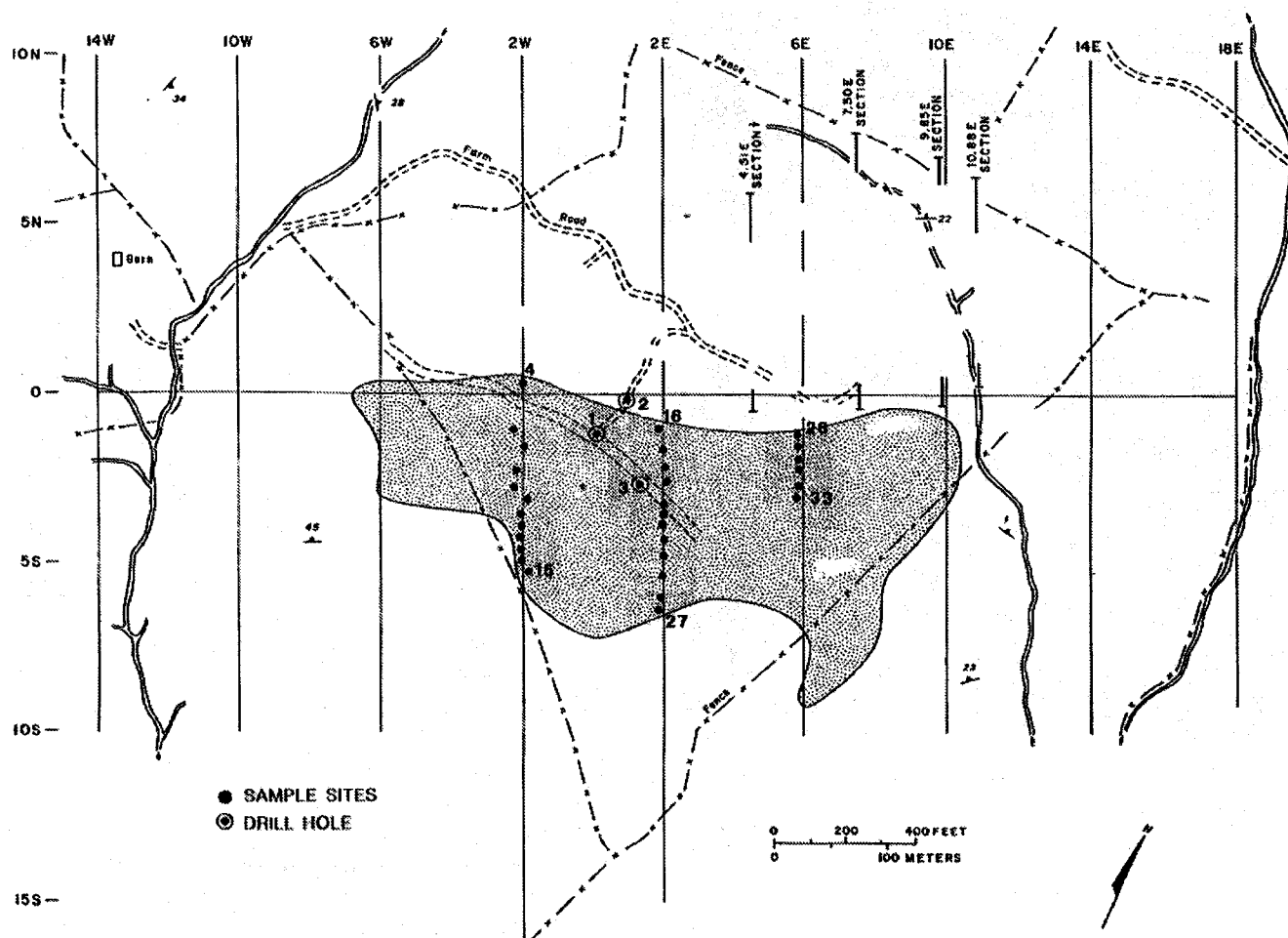


Figure 9. Detailed location of 3 drill holes, Zone 24, Buckingham County.



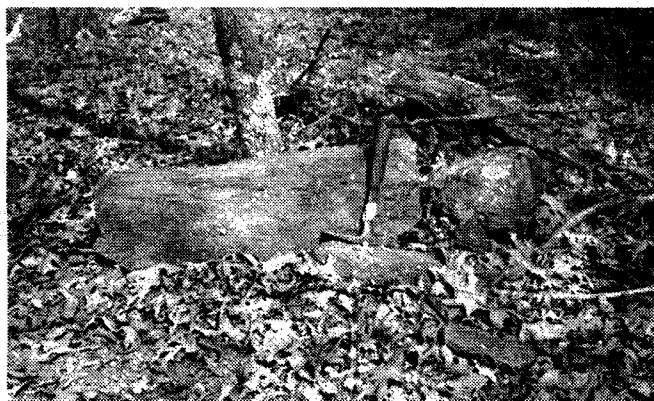


Figure 10. Large pieces of gossan float near sample # 12 along line 1, Zone 24.

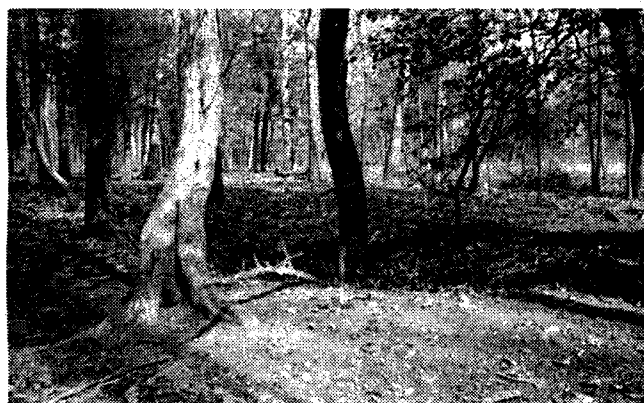


Figure 11. Old pit located near sample # 13, Zone 24.



Figure 12. Large pile of gossan, located just south of line 3 and sample # 33, Zone 24.

Table 3. Quantities of cadmium, gallium, germanium (all ppm), and silica (%) in sulfide Zones 18 and 24.

	Cadmium	Zone 18			Silica
		Gallium	Germanium		
1.	30	14	<10		13.2
2.	33	23	<10		10.2
3.	24	23	<10		25.9
Zone 24					
4.	21	19	10		36.1
5.	26	23	<10		15.6
6.	27	25	<10		18.1
7.	23	26	<10		27.8
8.	16	24	<10		41.9
9.	25	28	<10		24.8
10.	29	53	<10		16.2
11.	25	29	<10		23.4
12.	11	32	<10		43.6
13.	14	33	<10		37.7
14.	19	12	<10		31.3
15.	29	22	<10		18.1
16.	20	35	10		34.3
17.	20	26	<10		33.8
18.	15	27	<10		43.6
19.	13	28	10		38.7
20.	31	55	<10		12.2
21.	18	32	<10		31.0
22.	13	13	<10		39.9
23.	11	25	<10		41.6
24.	7	7	<10		63.8
25.	6	8	<10		61.0
26.	21	22	<10		28.9
27.	3	31	<10		61.3
28.	26	20	<10		23.1
29.	25	33	<10		14.2
30.	28	21	<10		17.3
31.	43	20	<10		14.6
32.	5	46	<10		75.4
33.	24	21	<10		24.8

Three vertical holes were drilled in Zone 24 to take sub-surface samples (Figure 8). Hole # 1 was drilled through about 40 feet of reddish-brown clay and the lower 10 feet in friable quartzite and weathered garnetiferous chlorite schist. Hole # 2 had 20 feet of reddish-brown clay at the top and friable quartzite and quartz sericite schist in the lower 20 feet; the hole bottomed in hard gossan. Hole # 3 was drilled through reddish-brown clay with some quartz stringers and minor quartz sericite schist in the top 46 feet; the lower 20 feet is mostly clay with several thin gossan zones, including one at the bottom of the hole. Samples for analyses were taken as a composite of every 1.5 feet down the hole; amounts of cadmium, gallium, germanium (all ppm) and silica (%) for each composite sample are shown in Tables 4 - 6.

Table 4. Quantities of cadmium, gallium, germanium (all ppm) and silica (%) in drill hole # 1 (50.75 feet TD).

	Cadmium	Gallium	Germanium	Silica
1.	<1	35	<10	54.9
2.	<1	41	<10	35.1
3.	<1	33	<10	67.7
4.	<1	39	<10	43.4
5.	1	52	<10	30.3
6.	<1	35	<10	45.1
7.	1	42	<10	53.6
8.	<1	31	<10	61.2
9.	<1	30	<10	61.6
10.	2	30	<10	57.4

Table 5. Quantities of cadmium, gallium, germanium (all ppm), and silica (%) in drill hole # 2 (41.1 feet TD).

	Cadmium	Gallium	Germanium	Silica
11.	<1	37	<10	51.6
12.	<1	37	<10	51.4
13.	<1	35	<10	45.0
14.	<1	28	<10	72.4
15.	<1	33	<10	56.9
16.	<1	32	<10	63.2
17.	<1	27	<10	74.7
18.	2	44	<10	42.7

Table 6. Quantities of cadmium, gallium, germanium (all ppm), and silica (%) in drill hole # 3 (66.5 feet TD).

	Cadmium	Gallium	Germanium	Silica
19.	<1	27	<10	55.7
20.	<1	32	<10	59.0
21.	<1	30	<10	62.8
22.	<1	28	<10	56.2
23.	<1	26	10	72.3
24.	<1	32	<10	59.2
25.	<1	35	<10	54.8
26.	<1	32	<10	52.7
27.	<1	30	<10	50.6
28.	<1	35	<10	46.9
29.	<1	32	<10	54.1
30.	<1	42	<10	67.6
31.	<1	39	<10	63.0

#### CADMIUM, GALLIUM, AND GERMANIUM IN COAL

The presence of gallium and germanium in coal was reported in the late 1940s and high concentrations of germanium (2500 ppm) were noted in the Lower Kittanning coal bed in Ohio (Kneller, 1986). The Virginia Division of Mineral Resources has sampled and analyzed 375 samples of coal

in southwest Virginia between 1975 and 1988 (Henderson and others, 1981; Henderson and others, 1985; Wilkes and others, 1992). Trace-element analyses were conducted by the U.S. Geological Survey, Branch of Geochemistry in Reston, Virginia and in their laboratory in Denver, Colorado. Coal samples from all the sites were ground and 25-75 grams were burned to an ash at 525 C; wet chemical analysis (atomic absorption) was utilized to analyze for cadmium, and optical emission spectrophotographic analysis was used to analyze for gallium and germanium. The highest values of cadmium, gallium, and germanium (all ppm) and the original coals are displayed in Table 7.

Table 7. Quantities of cadmium, gallium, and germanium in Virginia coals.

Element	Value	Coal bed
Cadmium	44 ppm	Jawbone-Tiller
Gallium	120 ppm	Clintwood
Germanium	300 ppm	Clintwood

#### CONCLUSIONS

Of the samples tested, only one at the Bowers- Campbell mine was anomalous. A sample of sphalerite in brecciated dolomite with greenockite (CdS) analyzed 3000 ppm of cadmium. Concentrations of germanium and gallium in coal ash offer as much promise as any of the zinc tailings, zinc ore or base-metal sulfide samples. Future potential may exist for extraction of Cd, Ga, and Ge from flyash. Approximately 1 million tons per year is produced by burning coal at power plants in Virginia (Sweet, 1994). Chemical analyses of flyash at the Virginia Power Company's Chesapeake power plant indicates only trace amounts of cadmium (J. Izard, 1995, personal communication).

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#### NEW RELEASE

**Publication 138** - Geologic Map of Warren County, Virginia, by Eugene K. Rader and James F. Conley, scale 1:50,000, full-color with explanation, one sheet. **Price: \$7.00**

#### TOPOGRAPHIC MAP PRICE INCREASE

Effective October 2, 1995, the price of 1:24,000 scale (7.5-minute) topographic maps will be **\$4.00**.